

Rough acetolysis rates were measured on 1-OTs and 1-OMs in sealed ampules containing 0.1 M 1 and 0.2 M NaOAc in 2% acetic anhydride in glacial acetic acid at 121.4 ± 0.3 °C, using the procedure of Young, Winstein, and Goering.²⁵ 1-OTs had a rate constant of 2.1×10^{-6} l./s mol and 1-OMs of 2.8×10^{-6} l./s mol.

The acetolysis of 1-OTf was followed by NMR analysis, using 0.44 M 1-OTf and 0.87 M NaOAc. The ester in acetic acid has a sharp singlet (¹⁹F NMR) at 7116 Hz above CFCl₃ while trifluoromethanesulfonate ion has one at 6787 Hz. Rate constants for acetolysis follow: at 60.0 ± 0.3 °C, 1.0×10^{-4} l./s mol; at 70.0 ± 0.3 °C, 4.1×10^{-4} l./s mol.

Acknowledgment. The authors are indebted to the National Science Foundation for generous support of this research under Grant GP 8913X.

Registry No.—1-OMs, 61436-65-5; 1-OTf, 61436-66-6; 1-OH, 6624-25-5; 1-OAc, 61394-44-3; 1-NH₂, 4053-27-4; 1-NH₃Cl, 6275-73-6; 1-OTs, 4427-38-7; 9-OH, 23445-14-9; 9-OAc, 24332-09-0; 10-OH, 23445-15-0; 10-OAc, 24332-08-9; 11-OAc, 24330-16-3; 12-OH, 61394-45-4; 12-OAc, 61394-46-5; 13-OH, 61394-47-6; 13-OAc, 61394-48-7; 14, 19978-14-4; 15, 30122-20-4; 16-OH, 59938-58-8; 16-OAc, 59938-57-7; methanesulfonyl chloride, 124-60-3; trifluoromethanesulfonyl anhydride, 358-23-6; 3,3-dichlorodibenzotricyclo[3.2.2.0^{2,4}]nonadiene, 6531-28-8.

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- (9) A number of investigators^{4,10} have suggested direct displacement by nucleophiles upon diazonium ions, and this was first demonstrated by Collins and Benjamin.^{10a}
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Mode of Formation of Deoxybenzoin in the Reaction of N-Benzyl- α -phenylnitrone with Potassium Hydroxide-*tert*-Butyl Alcohol

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Treatment of *N*-benzyl- α -phenylnitrone with potassium hydroxide-*tert*-butyl alcohol was found to give deoxybenzoin. The formation of the deoxybenzoin was found to be the result of base attack on an aldol type condensation product (7) of the nitrone. The latter compound could be formed in moderate yield, by treatment of the nitrone with lithium dimethylate. Treatment of the condensation product with potassium hydroxide-*tert*-butyl alcohol gave deoxybenzoin, benzoic acid, benzamide, benzyl alcohol, tetraphenylpyrazine, and a trace of benzaldehyde. A scheme is proposed to account for these products.

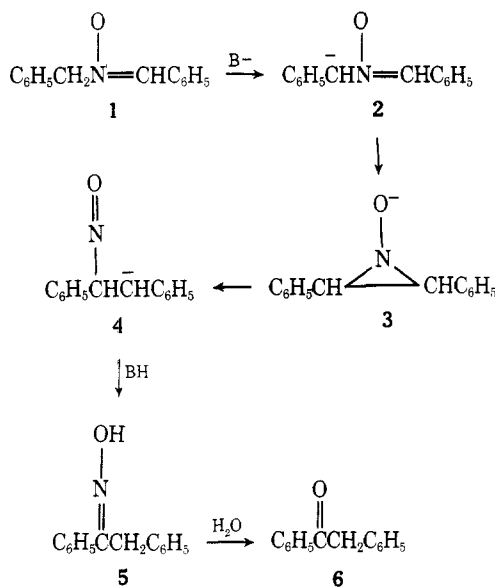
In connection with an entirely different investigation, we had occasion to treat tribenzylamine *N*-oxide with potassium hydroxide in *tert*-butyl alcohol, and obtained, among other products, the ketone, deoxybenzoin (6).¹ Since we obviously had chanced on to some type of rearrangement reaction, we undertook to determine the mode of formation of the deoxybenzoin.

The first clue to the deoxybenzoin formation was the isolation of a small amount of *N*-benzyl- α -phenylnitrone (1) from the above reaction mixture. With the thought that this nitrone might possibly be the precursor of the deoxybenzoin, we synthesized the nitrone in quantity, using a modification of the procedure reported by De La Mare and Coppinger.² Treatment of the *N*-benzyl- α -phenylnitrone with potassium hydroxide in refluxing *tert*-butyl alcohol did indeed give deoxybenzoin, along with a number of other products.

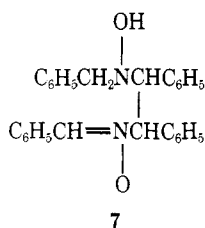
One of the possible mechanistic pathways for the formation of the deoxybenzoin from the nitrone is given in Scheme I. According to this scheme the anion of the nitrone undergoes ring closure to the anion of an *N*-hydroxyaziridine (3), which subsequently could undergo C-N bond cleavage to ultimately give deoxybenzoin oxime (5). The observed deoxybenzoin could then be formed on workup in aqueous solution. However, examination of the reaction products failed to reveal the presence of any of the oxime (5). Further, refluxing of an authentic sample of deoxybenzoin oxime with potassium hydroxide-*tert*-butyl alcohol, followed by the same workup of the reaction as used with the nitrone, gave only recovered oxime and no deoxybenzoin. This result apparently eliminates Scheme I.

A second clue to the deoxybenzoin formation was found when we succeeded in isolating from the nitrone (1), KOH,

Scheme I

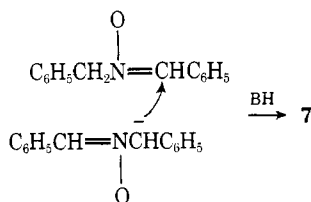


tert-butyl alcohol reaction a small amount of a solid, mp 196 °C. Elemental analysis suggested that this compound had the same empirical formula as the starting nitrone. That this product was a dimer was shown by its mass spectrum with the parent peak at *m/e* 422. Other peaks noted were at *m/e* 405, parent minus OH; 386, parent minus O and H₂O; 301, parent minus C₆H₅CHNOH; 211, C₆H₅CH₂NO=CHC₆H₅; 180, C₆H₅CH=CHC₆H₅; 121, C₆H₅CHNOH; 105, C₆H₅CN₂N; 103, C₆H₅CN; and 91, C₆H₅CH₂. On the basis of this data, and on the NMR and IR spectra, the compound was assigned the structure 7. The UV spectrum of 7 in chloroform exhibited a



peak at 298 nm, characteristic of the nitron linkage.³ Irradiation of the chloroform solution of 7 with UV caused disappearance of the 298-nm absorption as expected, since nitrones are known to be converted to oxaziridines under these conditions.³⁻⁵

Basically, 7 is an aldol type condensation product. A few other examples of nitrones undergoing an aldol type condensation have been reported.⁶⁻⁹ It was subsequently found that 7 could be formed in moderate yield by treatment of the nitrone 1 with lithium dimethylsulfate in dimethyl sulfoxide.

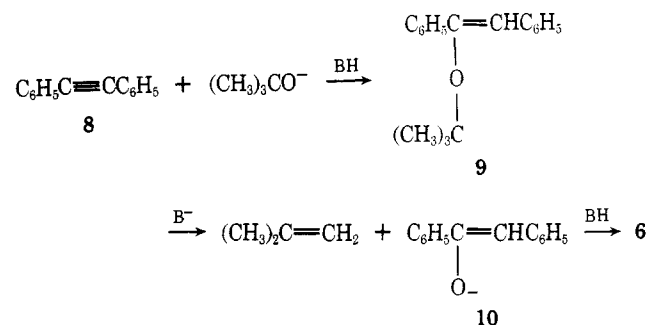


Treatment of the condensation product (7) with refluxing potassium hydroxide-*tert*-butyl alcohol was found to give a high yield of deoxybenzoin along with benzoic acid, benzamide, benzyl alcohol, tetraphenylpyrazine, and a trace of benzaldehyde. This observation revealed that the real pre-

cursor of the deoxybenzoin was the aldol type condensation product.

This opens the question as to the pathway by which 7 gives rise to deoxybenzoin. One possibility is that 7 is destroyed in the basic media and gives rise to diphenylacetylene, which subsequently adds water, perhaps as shown in Scheme II.

Scheme II



However, we were unable to isolate diphenylacetylene from the reaction mixture. Further, when diphenylacetylene was treated with potassium hydroxide in *tert*-butyl alcohol, we were unable to detect deoxybenzoin or isobutylene.

One possibility, which accounts not only for the formation of deoxybenzoin, but also explains the formation of most of the other observed products, is given in Scheme III. Hydrolysis of the nitron linkage, followed by the elimination of hydroxylamine, would give 11. Oxidation of 11 could be expected to give the nitron 12. Rearrangement of the nitron to the vinyl amide, followed by hydrolysis, would account for the formation of deoxybenzoin, benzoic acid, and benzamide. The benzyl alcohol and additional benzoic acid would be formed by the Cannizzaro reaction.

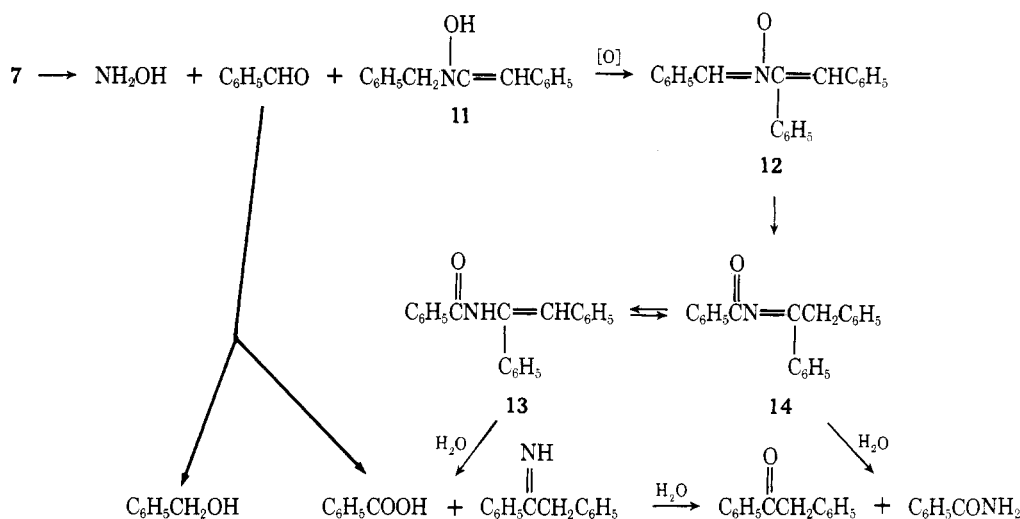
The alternative formation of 11 in a single step by elimination of benzaloxime from 7 can be discarded, since benzaloxime is not hydrolyzed under these conditions to benzaldehyde and consequently benzyl alcohol would not be a product. A second alternative involving the elimination of *N*-benzylhydroxylamine to give the nitron 12 directly can also be discarded. When *N*-benzylhydroxylamine was refluxed with potassium hydroxide-*tert*-butyl alcohol, no benzyl alcohol could be detected in the product.

Oxidation of 11 to 12 is apparently effected by peroxides in the potassium hydroxide. Oxygen can be excluded, since the reaction was run in an argon atmosphere.

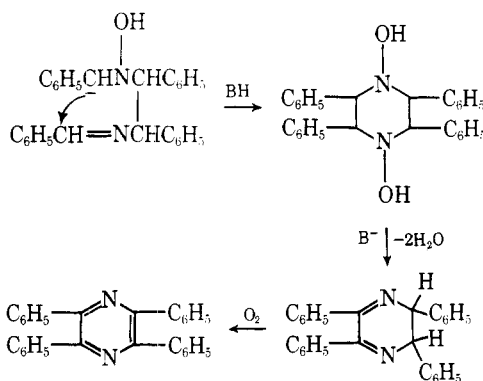
The rearrangement of nitrones to amides using sodium ethoxide was reported by Chardonnes and Heinrich,¹⁰ providing precedence for conversion of 12 to 13-14. The vinyl amide 13 is a known compound, and it has been reported to give deoxybenzoin 2,4-dinitrophenylhydrazone on treatment with 2,4-dinitrophenylhydrazine under acidic conditions.¹¹ Spectral evidence suggests that 13 exists as the vinyl amide rather than the tautomeric Schiff base 14.¹¹ However, in the basic media used here, both forms are probably present. Nucleophilic attack on the carbonyl of 13 would give rise to benzoic acid and the imine of deoxybenzoin. The latter would be hydrolyzed to the ketone during workup. Nucleophilic attack on the Schiff base 14 would give rise to benzamide and deoxybenzoin directly. Compound 13 was prepared and refluxed in *tert*-butyl alcohol containing potassium hydroxide. Workup of the reaction did indeed give benzoic acid, benzamide, and deoxybenzoin.

According to Scheme III, 1.0 mol of 7 should give rise to 1.0 mol of deoxybenzoin, 0.5 mol of benzyl alcohol, and 1.5 mol of benzamide plus benzoic acid. The isolated ratio of these products produced was found to be 1.0:0.48:1.6, in reasonable agreement with Scheme III.

Scheme III



The tetraphenylpyrazine, isolated in 4% yield, most likely arises by intramolecular aldol condensation of **7**, followed by elimination of water and air oxidation.



Experimental Section

***N,N*-Dibenzylhydroxylamine.** A modification of the procedure of De La Mare and Coppinger² was used. α -Chlorotoluene (63 g, 0.5 mol), hydroxylamine hydrochloride (17.4 g, 0.25 mol), and sodium carbonate (87 g, 0.82 mol) were refluxed in 1 l. of methanol-water (3:1) for 4 h. The solvent was removed under vacuum and the residue was triturated with chloroform. The chloroform extracts were dried over magnesium sulfate and then evaporated to give the crude product. Recrystallization from isooctane-ethanol (3:1) gave 28.6 g (53.7%), mp 123 °C (lit.² mp 123–124 °C).

***N*-Benzyl- α -phenylnitrone.** The following modification of the De La Mare and Coppinger² procedure was used. *N,N*-Dibenzylhydroxylamine (10.0 g, 0.047 mol) and *tert*-butyl hydroperoxide (5.0 g, 0.055 mol) were refluxed in 80 ml of benzene for 10 h. The solution was cooled and dried over magnesium sulfate. Removal of the solvent under vacuum gave the crude product. Recrystallization from benzene-petroleum ether (1:2) gave 6.0 g (60.5%), mp 82° (lit.² 82–83 °C).

Reaction of *N*-Benzyl- α -phenylnitrone with Potassium Hydroxide in *tert*-Butyl Alcohol. In 50 ml of *tert*-butyl alcohol were placed 10 g of powdered potassium hydroxide and 2.00 g (9.50 mmol) of *N*-benzyl- α -phenylnitrone. The heterogeneous mixture was refluxed for 8 h. Most of the *tert*-butyl alcohol was removed under vacuum at 70 °C. The residue was treated with ice water and the resulting mixture dried over magnesium sulfate and then evaporated to give 1.24 g of organic material. The aqueous layer was acidified and extracted with chloroform. The extracts were dried over magnesium sulfate. Evaporation of the chloroform gave 0.79 g of benzoic acid, contaminated with a trace of benzaldehyde, as shown by the NMR spectrum.

The 1.24 g of neutral material from above was redissolved in chloroform and placed on a basic alumina column (Camag 5016-A). Elution with chloroform gave the following fractions: A, 0.120 g; B, 0.477

g; C, trace; D, 0.475 g. Elution with methanol gave fraction E, 0.170 g.

Fraction A was recrystallized from absolute ethanol to give a white solid, mp 249 °C. The NMR and IR showed only aromatic protons. The compound was identified as tetraphenylpyrazine by its spectral properties, elemental analysis, and reported melting point (lit.¹² 249–250 °C), yield 7%.

Fraction B was a solid, mp 53–55 °C, identified as deoxybenzoin by IR, NMR, and mixture melting point with an authentic sample, yield 51.4%.

Fraction D was a liquid identified as benzyl alcohol by NMR and IR, yield 46.3%.

Fraction E was found to be benzamide by NMR, IR, and mixture melting point, yield 14.8%. After recrystallization from benzene, it melted at 129 °C.

Aldol Condensation Product (7) from Treatment of *N*-Benzyl- α -phenylnitrone with Lithium Dimethylsulfate. To 20 ml of dimethyl sulfoxide (spectroquality, 99.85%) in an argon atmosphere was added 3.00 ml of 1.66 M *n*-butyllithium (5.00 mmol). After 10 min, 2.00 g (9.50 mmol) of *N*-benzyl- α -phenylnitrone was added all at once. The mixture was stirred at room temperature under an argon atmosphere. The mixture turned a deep purple and then to a dark brown after 10 min. After 30 min, the reaction mixture was diluted with water (color changed to bright yellow) and the product extracted with chloroform. The extracts were dried over magnesium sulfate. Evaporation of the solvent gave 2.00 g of solid residue. Recrystallization from alcohol gave 0.60 g (30%) of **7**, mp 196 °C. See text for spectral data (UV and mass). NMR (Hz) 217, m (broad), 2-H; 247, s, 2-H; 324, s, 1-H; 433, m, 20-H; 460, s, 1-H. IR (cm⁻¹) 5000 (OH), 1575 (C=N), and 1280 (N-O).

Anal. Calcd for C₂₈H₂₆N₂O₂: C, 79.59; H, 6.15; N, 6.63; mol wt, 422. Found: C, 79.42; H, 6.24; N, 6.56; mol wt, 422.

Reaction of Aldol Condensation Product (7) with Potassium Hydroxide in *tert*-Butyl Alcohol. In 50 ml of *tert*-butyl alcohol were placed 12 g of finely powdered potassium hydroxide and 2.00 g (4.74 mmol) of the aldol condensation product, **7**. The mixture was refluxed for 5 h. Most of the alcohol was removed under vacuum at 70 °C. The residue was treated with ice water and the product extracted with chloroform. The extracts were dried over magnesium sulfate and evaporated under vacuum, to give 1.38 g of neutral products.

The aqueous layer was acidified and extracted with chloroform. After drying over magnesium sulfate, the extracts were evaporated to give 0.57 g (0.048 mol) of benzoic acid, containing a trace of benzaldehyde.

The neutral fraction (1.38 g) was separated on a basic alumina column (Camag 5016-A) to give the following fractions: A, 0.082 g; B, 0.672 g; C, 0.273 g; D, 0.180 g; E, 0.103 g. Fractions A–D were eluted with chloroform and fraction E with methanol. A was tetraphenylpyrazine, mp 249 °C, yield 4%; B was deoxybenzoin, mp 53–55 °C, yield 72%; C was a mixture of unidentified materials; D was an oil and was identified (IR, NMR) as benzyl alcohol, yield 72%; and E was benzamide, yield 18%.

Reaction of 13 with Potassium Hydroxide in *tert*-Butyl Alcohol. The procedure above was repeated using 1.00 g of **13**.¹¹ Workup

as above gave benzamide, 0.17 g; benzophenone, 0.48 g (purified as the 2,4-dinitrophenylhydrazone); benzoic acid, 0.12 g; and unreacted 13, 0.09 g.

Reaction of *N*-Benzylhydroxylamine with Potassium Hydroxide in *tert*-Butyl Alcohol. The procedure above was repeated using 1.00 g of *N*-benzylhydroxylamine.¹³ The neutral fraction was examined by IR and NMR and found to contain neither benzaldehyde nor benzyl alcohol.

Acknowledgment. We would like to thank Dr. Cal Meyers, whose work on the *tert*-butyl alcohol-potassium hydroxide system inspired much of this work.

Registry No.—7, 61267-53-6; dimethyl sulfoxide, 67-68-5; *N*-benzyl- α -phenylnitron, 3376-26-9; *tert*-butyl alcohol, 75-65-0; potassium hydroxide, 1310-58-3; tetraphenylpyrazine, 642-04-6; deoxybenzoin, 451-40-1.

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Thermal Decomposition of 1-Phenyl-3,3-ethylenetriazenes¹

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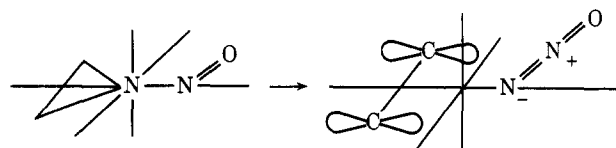
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Upon warming to room temperature, *cis*- or *trans*-1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene decomposes to form *cis*- or *trans*-2-butene and phenyl azide with retention of configuration. The decomposition reaction is first order, with an activation energy of 32 kcal/mol. Low-temperature NMR studies suggest that there is a hindered rotation in the *trans* compound with an activation energy of 5.7 kcal/mol. A mechanism has been proposed for the decomposition reaction that is consistent with orbital symmetry rules.

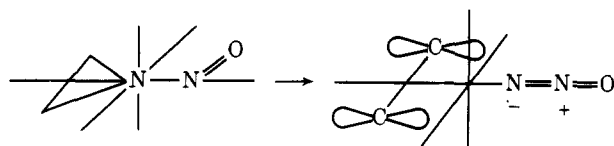
Ethylenediazene and *N*-nitrosoaziridine have been reported to be unstable, decomposing below room temperature to form ethylene and the corresponding inorganic compound.² In both cases the reaction has been reported to be stereospecific with retention of configuration.^{2a,3}

Woodward and Hoffman⁴ have considered these two systems from the viewpoint of orbital symmetry. They concluded that both reactions proceed by a nonlinear pathway in which the nonbonding electron pair on the nitrogen atom originally in the ring comes from the antisymmetric molecular orbital of the triazene. In the case of the nitrosamine, they recognized two possible pathways by which this could take place. In the first pathway (mechanism A), the nitrous oxide molecule was



Mechanism A

visualized as leaving orthogonal to the plane bisecting the aziridine ring. In the second pathway (mechanism B), the

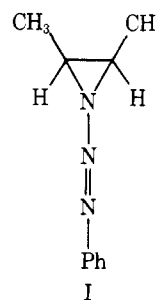


Mechanism B

nitrous oxide molecule was visualized as remaining in the plane bisecting the aziridine ring.

With little direct experimental data available, Woodward and Hoffman suggested that mechanism A was more probable than mechanism B. This suggestion was based on the observation that the barrier to rotation in dimethylnitrosamine is 23 kcal/mol⁵ while the barrier to decomposition of *trans*-2,3-dimethyl-*N*-nitrosoaziridine is only 16 kcal/mol.^{2a} To the extent that it is valid to extrapolate from dimethylnitrosamine to *N*-nitrosoaziridine, it appears that the compound would decompose before it could achieve the correct conformation for mechanism B.

Because of the lack of direct experimental evidence concerning the difference between mechanisms A and B, we felt that it would be enlightening to investigate another cheletropic three membered ring decomposition. We chose the thermal decomposition of 1-phenyl-3,3-(2,3-dimethyl)ethylenetriazene (I) because it could be isolated and purified, it



decomposed readily, and no stereochemical or mechanism work had been reported.

Preparation of 1-Phenyl-3,3-(2,3-dimethyl)ethylenetriazene. Phenyl-substituted ethylenetriazenes were first reported by Rondestvedt and Davis,⁶ who found that they were unstable, decomposing to form ethylene and phenyl azide